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PRINCIPLES OF POLYMER PROCESSING

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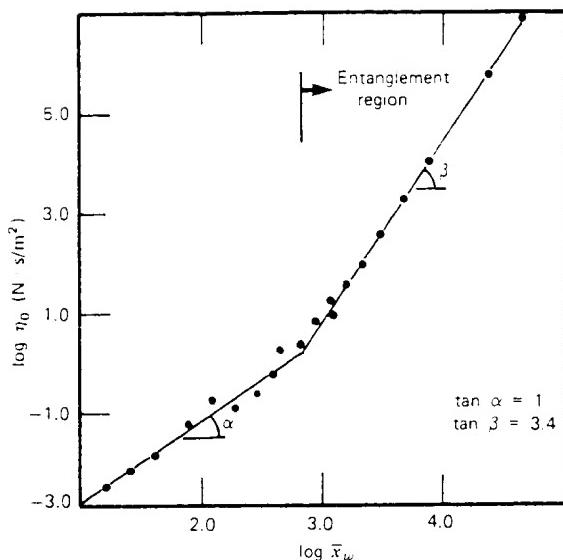


Fig. 2.3 The dependence of the zero shear rate viscosity on the weight average chain length for polyisobutylene at 217°C. [Reprinted with permission from T. G. Fox, S. Gratch, and S. Loshaek, in *Rheology*, Vol. 1, F. R. Eirich, ed., Academic Press, New York, 1956, Chapter 12.]

bonding, *chain entanglements* may contribute to keeping macromolecular aggregates together and may affect their properties. Thus the break in the zero shear viscosity versus molecular weight curve in Fig. 2.3 is attributed to the onset of the entanglement phenomenon.

The degree to which intermolecular forces are utilized depends on the distance between the chemical entities partaking in the bonds, since to a first approximation these forces decrease with the inverse seventh power of this distance. We should, therefore, discuss the states in which polymers find themselves that are characterized by different values of specific volume and macromolecular order (conformations). There are two classes of polymer: those that are almost totally *amorphous* and those that are *semicrystalline*. Amorphous polymers are composed of chains that are randomly packed and are characterized by a major second order transition, the glass transition temperature, where they change from brittle, glassy solids to rubberlike substances. Below T_g the random coil chains are rigid, whereas above it they are flexible. Semicrystalline polymers, below their melting temperature, form both amorphous and crystalline regions. The amorphous regions respond to temperature as described earlier. The crystalline regions are crystallite (folded chain) aggregates, usually in the morphology of *spherulites*. Figure 2.4 gives a micrograph of spherulitic morphology. Polymer molecules have different polarizabilities along and across the chain. Since the chains are perpendicular to the spherulite radii, such aggregates are *birefringent* and scatter light if they are of a size comparable to the wavelength of visible light (cf. amorphous polymers, e.g., PS, which are optically clear). The size of spherulites affects not only the optical properties of polymers, but also their mechanical response and diffusional properties. The percentage of crystallinity, the number and size of spherulites, and the

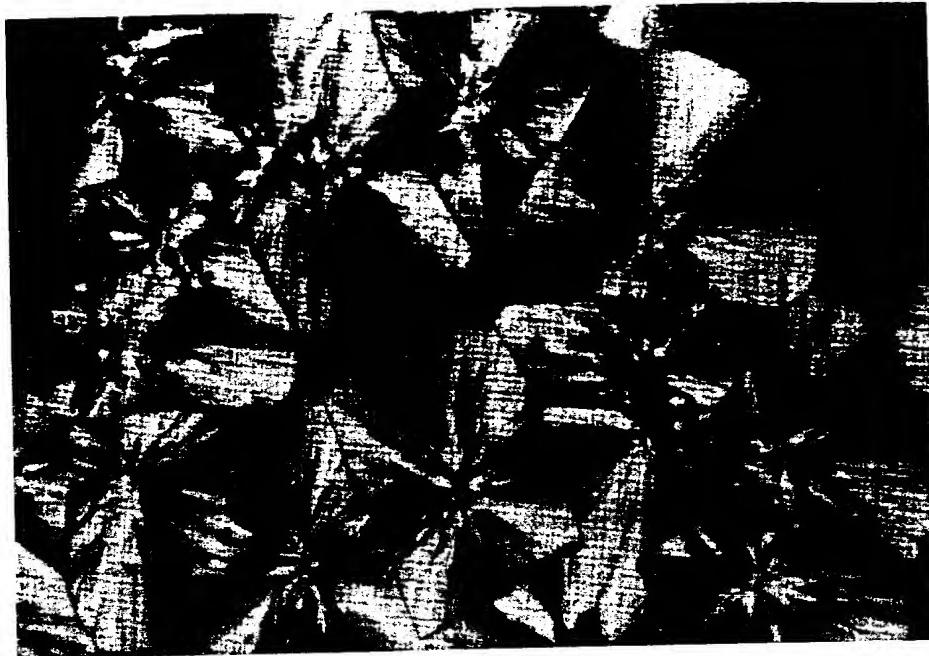


Fig. 2.4 Spherulitic morphology of isotactic polypropylene viewed through a polarizing microscope, $\times 200$.

rate of crystallization depend strongly on the crystallization (annealing) temperature as well as the degree of macromolecular orientation during crystallization, brought about by the application of a stress field. Thus again polymer processing affects polymer properties by affecting the morphology of a processed sample. Chapter 3 deals with the effects of processing on the properties and macrostructure of polymers. Crystalline morphologies other than spherulitic, which is the most common in commercial polymers and plastics, are polymer single crystals formed by folded chains and nonspherulitic morphologies obtained in polymers that contain nucleating agents or are crystallized at high degrees of supercooling.

Figure 2.5 gives the specific volume versus temperature curves for both amorphous and semicrystalline polymers, and Table 2.1 lists the glass transition temperature and melting point of some common polymers, together with their uses. The values of T_g and T_m relative to room temperature can be used together with structural properties to classify polymers as indicated below:

1. *Elastomers* are polymers with crosslinks, or intense entanglements, or microcrystalline regions, whose T_g is such that $T_g + 75^\circ\text{C} \leq T_{\text{room}}$.
2. *Glassy* polymers are amorphous substances whose T_g is such that $T_g \geq T_{\text{room}} + 75^\circ\text{C}$.
3. *Semicrystalline* polymers are substances of 50–90% crystallinity whose T_g is much below and T_m much above T_{room} .
4. *Fibers* are highly crystalline polymers that can be easily oriented with a T_m such that $T_m > T_{\text{room}} + 150^\circ\text{C}$.

Glassy and semicrystalline polymers as categorized above form the class of materials usually referred to as *plastics*. Some polymers (e.g., nylon 6, PP, PET) are used, either as plastics or as fibers.

As mentioned previously, polymer molecules in all the amorphous states—glassy, rubbery, molten, and solution—can be ideally treated by assuming that they

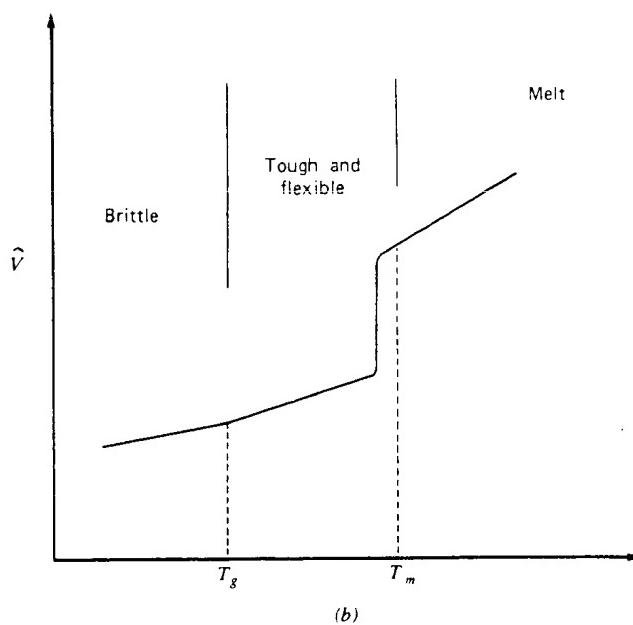
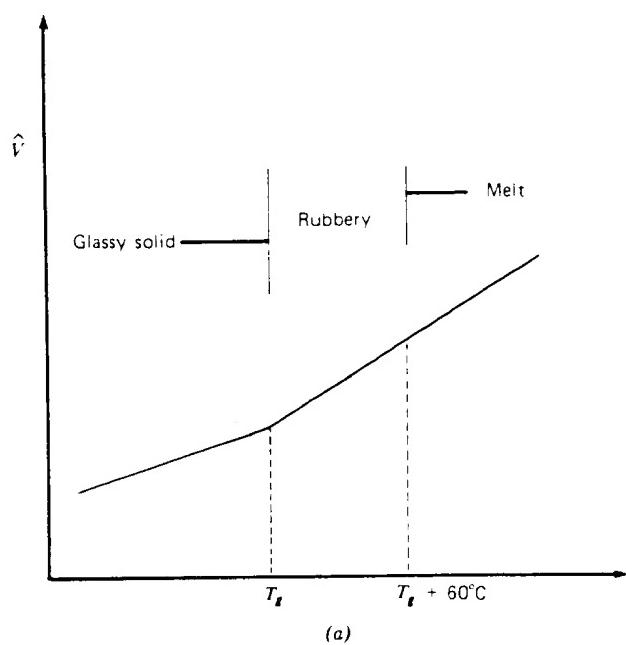


Fig. 2.5 The temperature dependence of the specific volume of polymers. (a) Amorphous. (b) Semicrystalline.